Synthesis of 9-Arylanthracenes

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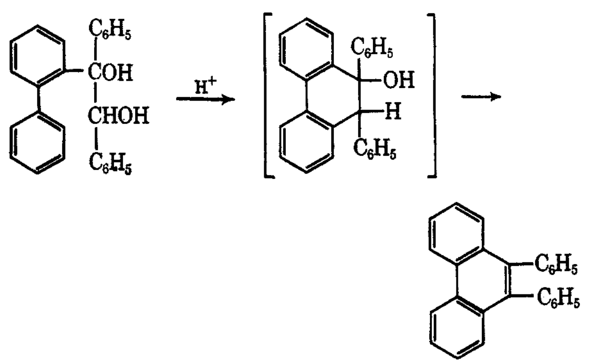
o-Diaroylbenzenes are converted to 9-arylanthracenes by sodium borohydride reduction, followed by aromatic cyclodehydration.

Aromatic cyclodehydration is a well-established synthetic method for the preparation of a variety of aromatic compounds.[1] In principle, the reaction involves using a starting material which yields a hydroxycarbonium ion on treatment with acid. Subsequent internal alkylation of an aromatic ring yields an intermediate which then aromatizes by dehydration. Of particular pertinence to the present work is the use of a vicinal glycol, as shown in eq 1.[2] Epoxides are also useful starting materials[1] and presumably provide the same intermediate as a vicinal glycol in acid media.

Transannular cyclodehydration to yield aromatic compounds is also well known (eq 2). However, the use of glycols in aromatic transannular cyclodehydration reactions has apparently been only little studied. Two examples reported[3,4] are shown in eq 3. It is interesting to note that phthalans can also serve as starting materials[4] analogous to epoxides in the case of vicinal glycols.



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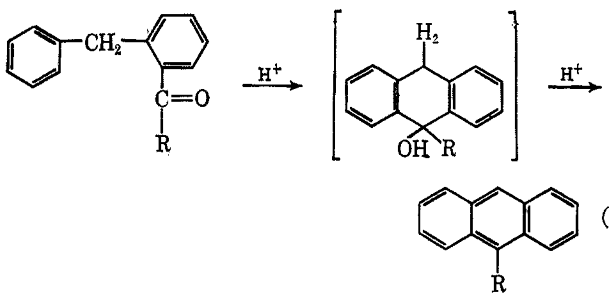
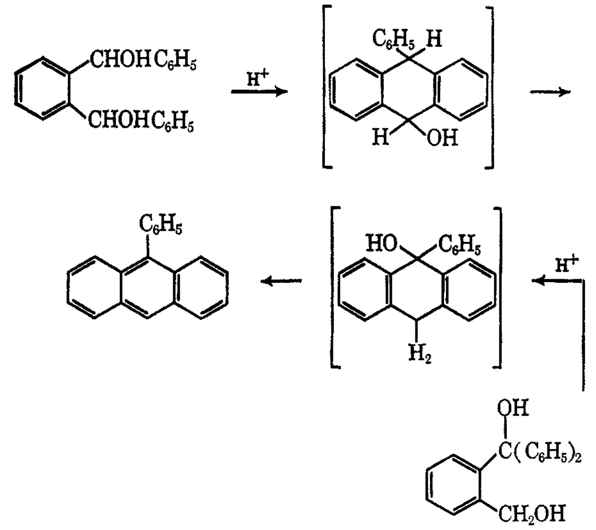


(2)



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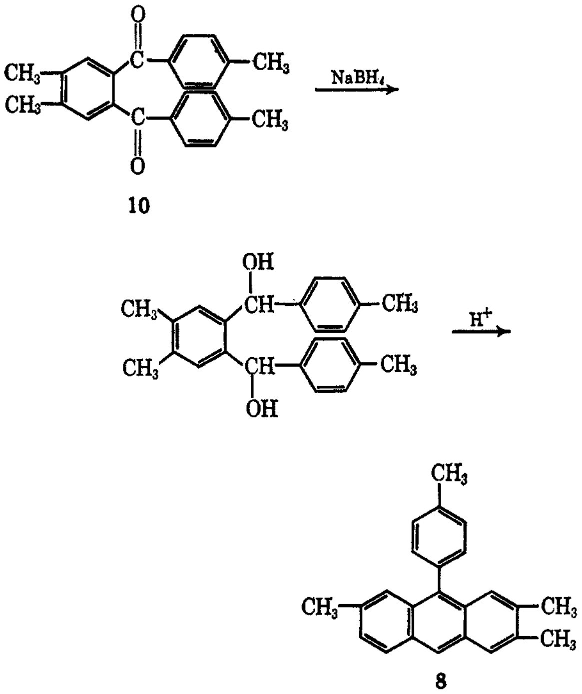
We have investigated the synthesis of 9-arylanthracenes (see Table I) by aromatic transannular cyclodehydration, an example of which is shown in eq 4.



(4)

o-Diaroylaromatics were prepared by published methods[5] and by the Diels–Alder reaction of dibenzoylacetylene with cyclopentadienones (Table II).

The diaroyl compounds were then reduced to glycols by using an excess of sodium borohydride in boiling bis(2-methoxyethyl) ether (diglyme). These rather drastic conditions were used in an attempt to ensure complete reduction and the absence of any 3-hydroxy-1,3-dihydroisobenzofurans.[6] On treatment with acid, such hydroxydihydroisobenzofurans yield isobenzofurans.[7] As shown in eq 5, such a product was obtained in a case where an excess of sodium borohydride was used in

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[1] C. K. Bradsher, *Chem. Rev.*, **38**, 447 (1946).

[2] C. K. Bradsher and L. J. Wissow, *J. Am. Chem. Soc.*, **65**, 2304 (1943).

[3] A. Guyot and J. Catel, *Bull. Soc. Chim. France*, **35**, 1121 (1906).

[4] A. Guyot and J. Catel, *ibid.*, **35**, 567 (1906).

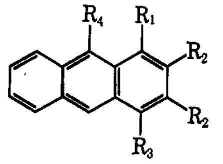
[5] The following compounds were prepared by methods given in the literature: (a) 1,2-dibenzoyl-3,6-dimethylbenzene (**11**) [R. Adams and T. A. Geissman, *J. Am. Chem. Soc.*, **61**, 2083 (1939)]; (b) 1,2-dibenzoyl-4,5-dimethylbenzene (**12**) [R. Adams and M. H. Gold, *ibid.*, **62**, 56 (1940)]; (c) 1,2-dibenzoyl-3,6-diphenylbenzene (**13**) [W. Ried and K. H. Bonnighausen, *Ann.*, **639**, 61 (1961)]; (d) 1,2-dibenzoyl-4,5-diphenylbenzene (**14**) [C. F. H. Allen and J. W. Gates, Jr., *J. Am. Chem. Soc.*, **65**, 1283 (1943)]; and (e) 1,2-di-*p*-toluyl-4,5-dimethylbenzene (**10**) [R. Adams and R. B. Wearn, *ibid.*, **62**, 1233 (1940)].

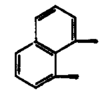
[6] H. H. Freedman and G. A. Doorakian, *Tetrahedron*, **20**, 2181 (1964).

[7] M. P. Cava, M. J. Mitchell, and A. A. Deana, *J. Org. Chem.*, **25**, 1481 (1960).

TABLE I

9-ARYLANTHRACENES

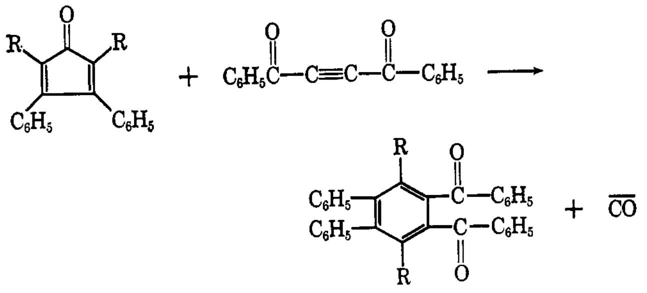


Product	Reactant	R₁	R₂	R₃	R₄	Yield,[b] %	Mp, °C	Formula	C, % Calcd	C, % Found	H, % Calcd	H, % Found
1	**11**	Me	H	Me	C_6H_5	27	127.5–129.5	$C_{22}H_{18}$	93.6	93.9	6.4	6.0
2	**12**	H	Me	H	C_6H_5	36	170–172.5	$C_{22}H_{18}$	93.6	93.4	6.4	6.8
3	**13**	C_6H_5	H	C_6H_5	C_6H_5	47	172–174	$C_{32}H_{22}$	94.6	94.9	5.4	5.2
4	**14**	H	C_6H_5	H	C_6H_5	43	189–190.5	$C_{32}H_{22}$	94.6	94.6	5.4	5.3
5	**15**	CH_3	C_6H_5	CH_3	C_6H_5	32	203–204.5	$C_{34}H_{26}$	94.0	93.8	6.0	6.7
6	**16**	C_2H_5	C_6H_5	C_2H_5	C_6H_5	41	235–236	$C_{36}H_{30}$	93.5	93.5	6.5	6.3
7	**17**	n-C_3H_7	C_6H_5	n-C_3H_7	C_6H_5	35[c]	178–179	$C_{38}H_{34}$	93.1	93.2	6.9	7.0
8[a]	**10**	H	CH_3	H	p-$C_6H_4CH_3$	58	177.5–180	$C_{24}H_{22}$	92.8	92.7	7.1	7.3
9	**19**	C_6H_5		C_6H_5	C_6H_5	45	315.5–319.5	$C_{42}H_{26}$	95.1	94.8	4.9	5.2

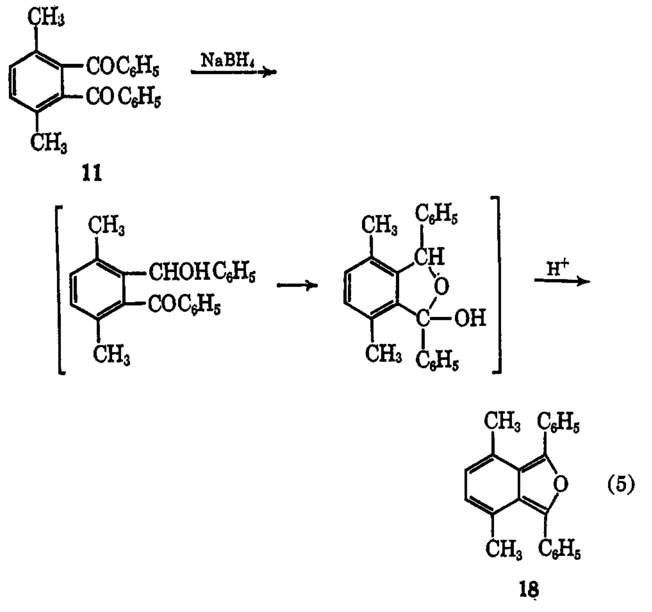
[a] Compound **8** also has a 7-methyl group. [b] Based on diaroyl starting material. [c] Also isolated 2.4% yield of 1,3,5,6-tetraphenyl-4,7-dipropylphthalan, mp 261–262°. *Anal.* Calcd for $C_{38}H_{36}O$: C, 89.5; H, 7.1. Found: C, 89.2; H, 6.7.

TABLE II

PREPARATION OF 1,4-DIALKYL-2,3-DIBENZOYL-5,6-DIPHENYLBENZENES



Product	R	Yield, %	Mp, °C (recrystn solvent)	C, % Calcd	C, % Found	H, % Calcd	H, % Found
15	CH_3	93	262.5–264 (AcOH)	87.6	87.4	5.6	5.8
16	C_2H_5	90	222–224 (EtOAc, C_6H_6–ligroin)	87.5	87.6	6.1	6.4
17	n-C_3H_7	79	178.5–179.5 (C_6H_6–ligroin)	87.4	87.3	6.5	6.2



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(5)

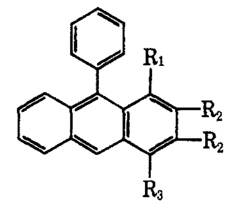
boiling ethanol. The glycols obtained by sodium borohydride reduction were isolated if they were crystalline, or were used in chloroform solution if syrupy. Even when isolated, however, they were not ordinarily characterized, owing to the presence of mixed isomers and to the reported instability of an example of this class of compounds.[5a]

In searching for a general procedure to effect the aromatic cyclodehydration, the most serious "side reaction" encountered was the formation of phthalans. Thus, although hydrogen bromide in acetic acid was suitable for preparing **2**, it favored phthalan in attempted preparation of **3**. The conversion of a phthalan to an anthracene was, however, demonstrated, and it seems probable that phthalans are the kinetic products, whereas anthracenes are the thermodynamic products of the reaction. If this is true, the conditions which gave phthalans might be expected to yield anthracenes with longer reaction times. The use of sulfuric acid is not preferred, since water-soluble products, presumably sulfonic acids, result unless the experimental conditions are carefully controlled. Although optimum conditions were not defined, a mixture of acetic acid and acetyl chloride was the most generally applicable reagent found. It was demonstrated, however, that phthalan formation remained a problem. Crude yields were generally good, but large losses in recrystallization were not infrequent.

Table III reports the ultraviolet and nmr data for these compounds. It is of interest to note that no appreciable changes in wavelengths of absorption or extinction coefficients in the 350–400-mμ region are occasioned in going from **2** to **4**. Since this region represents absorption by the anthracene portion of the molecule, it suggests little or no conjugation with the pendant phenyl groups. This same spectral consistency at longer wavelengths, together with a bathochromic shift at shorter wavelengths, is found in the data for 2,3,9,10-tetramethylanthracene *vs.* 2,3,9,10-tetraphenylanthracene.[8]

Table III

Ultraviolet and Nmr[a] Spectra of Anthracenes



Compd	$\lambda_{max}^{CHCl_3}$ mμ (log ε)	δ, ppm				
		R_1	R_2	R_3	9-C_6H_5	10-H
1	265 (4.88), 360 (3.81), 379 (4.00), 399 (3.95)	1.97	....	2.78	7.42	8.63
2	264 (5.06), 354 (3.76) 371 (3.92), 393 (3.88)	.....	2.25 2.37	....	7.43	8.22
8	266 (5.06), 358 (3.72), 374 (3.85), 394 (3.82)	.....	....	....	.....	....
3	269 (4.86), 368 (3.85), 385 (4.04), 404 (4.02)	6.92[c]	....	7.55	6.98[c]	8.85
4	293 (4.90), 361 (3.79), 380 (3.93), 401 (3.83)	.....	7.12 7.30	....	7.47	....
6	274 (4.88), 367 (3.78), 385 (3.95), 406 (3.87)	.....	6.98 7.05	....	7.45	8.83
7	275 (5.01), 367 (3.88), 385 (4.05), 406 (3.97)	.....	6.97 7.03	....	7.47	8.80
9[b]	288 (4.68), 295 (4.68), 328 (4.60), 343 (4.84), 387 (3.80), 405 (4.09), 427 (4.27), 453 (4.17)					

[a] The nmr spectra of these compounds will be reported in detail elsewhere by T. H. Regan and J. B. Miller. [b] The reported data for naphtho[2,3-*k*]fluoranthene, the parent compound, are: 256 mμ (log ε 4.80), 268 (4.74), 277 (4.70), 287 (4.77), 298 (4.60), 320 (4.77), 334 (5.07), 364 (3.86), 390 (4.00), 413 (4.14), 438 (4.14) [E. Clar, "Polycyclic Hydrocarbons," Vol. 2, Academic Press Inc., New York, N. Y., 1964, p 325]. [c] These assignments are arbitrary and may be transposed.

The nmr data will be commented on elsewhere but it is of interest that the absorption of the 1-phenyl protons in **3** is shifted about δ 0.6, owing to a "cyclophane effect" similar to that reported in the case of 1,8-diphenylnapthalene.[9]

Experimental Section

1,4-Dialkyl-2,3-dibenzoyl-5,6-diphenylbenzenes (Table II).—A mixture of 0.1 mole of the cyclopentadienone,[10] 0.1 mole of dibenzoylacetylene, and 60 ml of *o*-dichlorobenzene was heated to boiling, with stirring. The mixture was cooled and diluted with 250–400 ml of methanol which precipitated the product in nearly pure form. Recrystallization from the solvents listed in Table II afforded analytical samples.

8,9-Dibenzoyl-7,10-diphenylfluoranthene (**19**).—A mixture of 15.0 g (0.0422 mole) of 7,9-diphenyl-8-cyclopent[*a*]acenaphthylen-8-one (acecyclone),[11] 21.7 g (0.0926 mole) of dibenzoylacetylene, and 75 ml of *o*-dichlorobenzene was heated to boiling. An additional 10 g of dibenzoylacetylene was then added. After the solution had cooled, 125 ml of ligroin (bp 30–60°) was added and the mixture was filtered. The resulting solid was boiled with 100 ml of ethanol and the hot suspension was filtered, to yield 22 g of crude product, mp 256.5–257.5°. Recrystallization from 1.5 l. of ethyl acetate gave 11.7 g of product, mp 283–285°. Further recrystallizations from chloroform-ligroin (bp 30–60°), benzene, and acetic acid were necessary to obtain an analytical sample, mp 282.5–284.5°.

Anal. Calcd for $C_{42}H_{26}O_2$: C, 89.6; H, 4.6. Found: C, 89.5; H, 5.1.

1,2-Bis(α-hydroxybenzyl)-3,6-diphenylbenzene.—To a suspension of 2.3 g (0.06 mole) of sodium borohydride in 150 ml of diglyme was added 13.1 g (0.03 mole) of 1,2-dibenzoyl-3,6-diphenylbenzene. The mixture was stirred for 30 min at room temperature and then heated to boiling. Cooling and diluting the solution with 500 ml of water gave a solid. The solid was washed with water until neutral and then twice with methanol to yield 12.5 g (94%) of product, mp 258.5–263.5°. Two recrystallizations from toluene gave pure material, mp 267–269.5°.

Anal. Calcd for $C_{32}H_{26}O_2$: C, 86.8; H, 5.9. Found: C, 86.6; H, 5.9.

9-Arylanthracenes. General Procedure.—A mixture of 0.1 mole of a 1,2-diaroylbenzene derivative, 0.2 mole of sodium borohydride, and 500 ml of diglyme was heated to boiling. The solution (or suspension) was then cooled and diluted with 3 l. of water. If a solid resulted, it was removed by filtration, washed, dried, and used in the next step. If an oil resulted, the mixture was extracted with chloroform. The chloroform extract was then washed and dried with sodium sulfate, and the solvent was removed under reduced pressure. This gave an oil contaminated with diglyme which was used in the next step.

The solid (or oil) was heated on a steam bath with a mixture of 300 ml of acetic acid and 300 ml of acetyl chloride. If, after 2.5 hr, the mixture was homogeneous, it was stripped and the resulting crude anthracene was recrystallized. If not homogeneous, 1 l. of acetic acid was added and the mixture was heated an additional 14 hr before being stripped.

2,3-Dimethyl-9-phenylanthracene (**2**).—In addition to the general procedure, the following method was used. 1,2-Dibenzoyl-4,5-dimethylbenzene (9.4 g, 0.03 mole) was reduced with sodium borohydride as described in the general procedure. The resulting sticky solid was crystallized from methanol-water, to yield 8.5 g of white solid, mp 124.5–144.5°, which was not further characterized.

To a solution of 5.4 g of the above solid in 25 ml of hot acetic acid was added 25 ml of 30% hydrogen bromide in acetic acid. This caused a solid to separate. The mixture was then boiled until it was homogeneous and water was added to the point of incipient opalescence. Cooling to room temperature, filtering, and washing gave 4.3 g (89.5% yield) of 2,3-dimethyl-9-phenylanthracene, mp 171–173°.

1,3-Diphenyl-4,7-dimethylisobenzofuran (**18**).—A mixture of 6.28 g (0.02 mole) of 1,2-dibenzoyl-3,6-dimethylbenzene,[5a] 1.52 g (0.04 mole) of sodium borohydride, and 100 ml of ethanol was stirred for 1 hr and then briefly boiled until it was homogeneous. After the mixture had cooled, it was diluted with 500 ml of water and extracted with 250 ml of chloroform. The chloroform extract was washed with water, dried with sodium sulfate, and evaporated to yield a pasty solid. This solid was dissolved in 75 ml of acetic anhydride, 7 drops of concentrated sulfuric acid was added, and the resulting mixture was boiled for 1 min. Addition of ice and stirring for several hours gave 4.69 g of a crystalline, bright yellow solid, mp 109–127°. Two recrystallizations from ethanol gave authentic 1,3-diphenyl-4,7-dimethylisobenzofuran, mp 125–131° (lit.[5a] mp 129–131°). This compound had the correct elemental analysis and showed the reported instantaneous reaction with maleic anhydride.[5a]

1,3,5,6-Tetraphenyl-4,7-diethylphthalan.—A mixture of 9.88

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(8) R. N. Jones, *Chem. Rev.*, **41**, 353 (1947).

(9) H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963).

(10) 1,4-Diethyl- (and dipropyl-) 2,3-diphenylcyclopentadienone [C. F. H. Allen and J. A. VanAllan, *J. Am. Chem. Soc.*, **72**, 5165 (1950)]; 1,4-dimethyl-2,3-diphenylcyclopentadienone [C. F. H. Allen and J. A. VanAllan, *ibid.*, **64**, 1260 (1942)].

(11) W. Dilthey, I. terHorst, and W. Schommer, *J. Prakt. Chem.*, **143**, 189 (1935).

g (0.02 mole) of 1,2-dibenzoyl-3,6-diethyl-4,5-diphenylbenzene, 1.52 g (0.04 mole) of sodium borohydride, and 100 ml of diglyme was heated to the boiling point and then cooled. Dilution with water gave a highly viscous gum which was separated by decantation and air dried on a porous plate. The gum was then dissolved in 75 ml of hot acetic anhydride. Cooling gave crystals. To this suspension was added 7 drops of concentrated sulfuric acid and the mixture was briefly boiled. Cooling gave white crystals which were separated by filtration and washed with methanol to yield 2.02 g of crude product. Recrystallization from acetic acid and then *n*-propyl alcohol gave an analytical sample of the phthalan, mp 254–258.5°.

Anal. Calcd for $C_{36}H_{32}O$: C, 90.0; H, 6.7. Found: C, 90.2; H, 6.3.

1,3,4,7-Tetraphenylphthalan.—A mixture of 5 g of 1,2-bis(α-hydroxybenzyl)-3,6-diphenylbenzene, 25 ml of 32% hydrogen bromide in acetic acid, and 25 ml of acetic acid was heated to boiling. Additional acetic acid was added until the mixture was homogeneous at the boiling point. Cooling to room temperature gave crystals which were removed by filtration. Washing with acetic acid and methanol gave 2.5 g of crude phthalan, mp 222.5–227°. Recrystallization from acetic acid gave an analytical sample of the title compound, mp 225.5–229°.

Anal. Calcd for $C_{32}H_{24}O$: C, 90.6; H, 5.7; mol wt, 424. Found: C, 90.2; H, 5.7; mol wt, 424 (mass spectrum).

This same reaction could be carried out by dissolving the glycol in acetic acid and briefly boiling it after adding 48% hydrobromic acid, 85% phosphoric acid, 55% hydriodic acid, concentrated sulfuric acid, or 90% formic acid.

1,4,9-Triphenylanthracene (3). A. From 1,3,4,7-Tetraphenylphthalan.—A mixture of 1.3 g of the phthalan, 10 ml of acetic anhydride, and 1 drop of concentrated sulfuric acid was boiled until it was just homogeneous. Hydrolysis gave a solid which, after recrystallization from acetic acid, afforded 0.68 g of 1,4,9-triphenylanthracene, mp 171.5–174°.

B. From 1,2-Bis(α-hydroxybenzyl)-3,6-diphenylbenzene.—In addition to the general procedure, the title compound was prepared as follows.

A mixture of 8.8 g (0.02 mole) of the glycol, 100 ml of acetic anhydride, and 4 drops of concentrated sulfuric acid was stirred for 5 min. The mixture was heated until it was homogeneous and then poured on ice. The resulting solid was dried, boiled with benzene, and filtered, to yield 0.65 g of unidentified white solid. The filtrate was evaporated and the resulting solid was recrystallized from acetic acid, to yield 5.01 g (62%) of crude 1,4,9-triphenylanthracene. Two recrystallizations from *n*-propyl alcohol gave pure material, mp 170–172.5°.

If this procedure is carried out with larger volumes of concentrated sulfuric acid, subsequent hydrolysis yields a homogeneous solution, presumably as a result of sulfonation of the product.

Alumina: Catalyst and Support. XXXII.[1] Aryl Migration Accompanying the Dehydration of 2-Phenylethanol-1-C^{14} and 2-*p*-Tolylethanol-1-C^{14} over Aluminas[2,3]

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The dehydration of 2-phenyl- and 2-*p*-tolylethanol-1-C^{14} over aluminas was studied at 348° with the purpose of determining the extent of aryl group migration from carbon atom 2 to 1. The catalysts were "acidic' alumina-A, prepared from aluminum isopropoxide, and alumina-B, (containing 1% Na^+), which was made by impregnating alumina-A with aqueous sodium carbonate. Dehydration reactions were also carried out with alumina-A in the presence of pyridine. Phenyl migration occurring during the dehydration of 2-phenylethanol varied from 1.1 to 8.3%, and in the case of 2-*p*-tolylethanol from 8.9 to 18.0%. Maximum isomerization occcurred when pyridine was added to the alcohol.

The neighboring group participation during dehydration of β-substituted propanols over alumina catalysts was previously reported from this laboratory.[5] Under "nonisomerizing" conditions the C_4 olefins obtained from isobutyl alcohol were composed of 11 to 23% of *n*-butylenes. The highest percentage of *n*-butylenes was obtained over alumina having the lowest intrinsic acidity. Similar results were obtained during the dehydration of 2-phenylpropanol. In the presence of the "nonacidic" alumina, 60% of the dehydration was accompanied by skeletal rearrangement leading to the formation of allyl- and propenylbenzene.

As an extension of this study 2-phenylethanol-1-C^{14} and 2-*p*-tolylethanol-1-C^{14} were passed over an alumina of a relatively high intrinsic acidity, (alumina-A) which was prepared from aluminum isopropoxide by the method previously reported[6] and over a doped alumina (alumina-B, containing 1% Na^+) which was made from alumina-A by impregnating it with sodium carbonate solution. Dehydration reactions were also made over alumina-A in the presence of pyridine. The experimental conditions and results are given in Table I (expt 3 and 6).

The two alcohols used in this study were synthesized by carbonation with $C^{14}O_2$ of the Grignard reagents of benzyl chloride and of *p*-methylbenzyl chloride, followed by the reduction of the respective acids with lithium aluminum hydride. The yields were 70% for 2-phenylethanol-1-C^{14} and 67% for 2-*p*-tolylethanol-1-C^{14}, based on the radioactivity of the barium carbonate.

The dehydration experiments were made at 348 ± 2° in a previously described flow system.[6] A 20% solution of 2-phenylethanol and 2-*p*-tolylethanol in *t*-butyl alcohol were used for dehydration. This was done in order to minimize secondary readsorption of the respective styrenes over the catalyst and thus decrease their possible polymerization. The contact time was adjusted by changing the hourly liquid space velocity to obtain about 50 to 70% conversion. (Table I) The side products of dehydration were ethylbenzene and *p*-tolylethane, respectively, amounting to about 4% each based on the styrenes produced. The hydrogenation occurred most probably through a hydrogen transfer reaction between the alcohols and arylalkenes, catalyzed by alumina.

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[1] For paper XXXI see H. Pines and C. T. Goetschel, *J. Catalysis*, in press.

[2] Paper X in the series of Dehydration of Alcohols. For previous paper see F. G. Schappell and H. Pines, *J. Org. Chem.*, **31**, 1965 (1966).

[3] This research was supported by the Atomic Energy Commission Contract AT(11-1)1096.

[4] On leave of absence from the Weizmann Institute of Science, Rehovoth, Israel, 1961–1964.

[5] J. Herling and H. Pines, *Chem. Ind.* (London), 984 (1963).

[6] H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **82**, 2471 (1960).